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APPLICANTS

Avecia Limited

TITLE

INK RECEPTIVE SUBSTRATES

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This invention relates to ink receptive substrates and to processes for their preparation and use, particularly in the field of ink jet printing.

In recent years there have been advances in printing technology that permit the production of high resolution colour images through ink jet printing. These advances make it possible for a user to record a colour image in a digital format, transfer the image to a computer, manipulate the image, and then print the image using an ink jet printer. Current digital imaging systems are now capable of producing near photographic quality colour images.

Improvements in the quality of colour images produced by ink jet printers have resulted from developments in the components of the ink jet printer, such as printing heads, as well as advances in the ink compositions used in the ink jet printers. As a result of these developments in colour ink jet printing, a new factor limiting the resolution and appearance of colour images produced by ink printers has emerged. This limiting factor is the ink receptive substrate on which the image is printed.

Use of uncoated paper as the substrate for ink jet printing produces less than optimum resolution because fibres in the paper cause the ink to "run" sideways. Additionally, uncoated papers are typically not glossy and therefore do not give photographic quality output.

In an attempt to improve the performance of paper used with ink jet printers, some manufacturers extrude a plastic layer on the surface of the paper. The extruded plastic layer can give enhanced gloss, smoothness, and general appearance and is typically coated with materials that help to prevent the ink from running.

A drawback of extruded plastic paper coatings is that they typically have little or no porosity or liquid absorptivity. Consequently, the surface of these papers remain wet to the touch for an extended period of time because the ink drying mechanism is mainly due to evaporation of the ink solvent. It may take ten minutes or more for the images to completely dry, depending on the temperature and humidity. Because of this lengthy drying time, each printed sheet must be removed from the printer tray and set out to dry to prevent smudging or carryover of the printed image onto the back side of the next printed sheet. Also, this extended period of wet ink on the paper surface makes it more likely that the ink will run, lowering image quality.

Another attempt to improve the performance of paper used with ink jet printers involves placing a coating containing a porous mineral on a support medium. The porous mineral enhances ink absorption and thereby reduces the ink dry times. For example U.S. 4,780,356 discloses a porous membrane coated ink absorbent paper created by

coating a mineral/binder combination on paper, in which the mineral particles themselves can absorb the ink.

U.S. 5,104,730 describes forming a silica layer on top of a porous coating, which is fabricated from porous particles in a polymeric binder. U.S. 5,264,275, discusses forming a two-layer coating in which a lower layer has a smaller pore size and an upper layer has a larger pore size.

U.S. 5,463,178 discloses forming a porous coating from pseudo-boehmite and then applying a scratch resistant uppermost layer of silica gel. U.S. 5,472,773 describes producing a high gloss porous coated paper by first casting a porous layer from a pseudo-boehmite containing liquid on a smooth plastic sheet. A paper backing is then applied to the porous layer. Finally, the plastic sheet is separated from the porous layer to reveal the coated paper.

Others have found that ink absorbent coatings for ink jet recording media can be prepared using coatings that are free from inorganic filler particles. For example U.S. 5,374,475 describes preparing a polymeric solution and then adding a non-solvent to create microscopically small polymer particles. This polymer solution containing the microscopically small polymer particles is cast on a support media and then heat-treated to evaporate the solvents. U.S. 5,759,639 describes membrane coated substrates prepared by a phase inversion technique which entails coating a polymeric dope solution onto a substrate. The coated substrate is then quenched in a non-solvent, such as water, to produce a microporous structure.

U.S. 4,877,688 describes ink receptive coatings prepared by applying a pre-polymerised emulsion polymer to a transparent support.

According to the present invention there is provided an ink receptive substrate comprising:

(i) a support material; and

(ii) a porous polymer layer on the support material obtained by polymerisation of a microemulsion on the support material;

wherein the microemulsion comprises a co-polymerisable surfactant.

Microemulsions are distinguished from conventional emulsions by their higher optical clarity, low viscosity, small domain size and thermodynamic stability. Conventional emulsions settle into discrete layers over time and are generally cloudy, of high viscosity, large domain size and low thermodynamic stability.

The microemulsion is preferably a polymerisable oil-in-water, water-in-oil, oil-in-oil or more preferably a bicontinuous microemulsion. In bicontinuous microemulsions, an organic liquid forms a first continuous phase, an immiscible second liquid forms a second continuous phase and the phases are intermingled such that the properties hereinbefore ascribed to a microemulsion are observed. Preferred bicontinuous microemulsions

comprise an aqueous phase, one or more addition-polymerisable water-immiscible organic materials (hereinafter referred to for convenience as "polymerisable oil") and one or more surfactants.

The immiscible second liquid is preferably an aqueous phase, typically water optionally containing a solute. The solute may be a liquid (for example a volatile organic solvent, e.g. propylene glycol, ethylene glycol monobutyl ether, diethylene glycol monobutyl ether or 2-(2-ethoxyethoxy)ethanol) or a solid, especially a water-soluble inorganic salt, e.g. NaCl, KCl, $Al_2(SO_4)_3$, $CaSO_4$, $MgSO_4$ and mixtures thereof.

When the aqueous phase is water containing a solute the appropriate concentration of the solute therein may be found by simple experiment.

The microemulsion preferably comprises:

(a) 5 to 95 parts, more preferably 10 to 80, especially 30 to 70 parts of aqueous phase;

(b) 1 to 75 parts, more preferably 10 to 70 parts, especially15 to 50 parts of polymerisable oil; and

(c) 0.1 to 70 parts, more preferably 1 to 30 parts of co- polymerisable surfactant;

wherein all parts are by weight and the number of parts (a) + (b) + (c) adds up to 100.

The above preference for the maximum amount of water being 80 or 70 parts arises because at higher levels of water the porous structure of the polymer layer formed from the microemulsion tends to collapse, thereby reducing the ability of the resultant media to absorb the ink.

The microemulsion preferably contains a free-radical initiator, although such an initiator may be omitted in circumstances where it is not necessary to initiate polymerisation of the microemulsion. For example, electron beam polymerisation of microemulsions may under some circumstances proceed without including a free-radical initiator in the microemulsion. When a free-radical initiator is present in the microemulsion it is preferably present in an amount of 0.01 to 10%, more preferably 0.1 to 5% by weight relative to the total weight of the microemulsion.

Further ingredients may be present in the microemulsion, e.g. biocides, organic solvents, fillers (e.g. porous fillers, including silicas and aluminas), colorants, mordants (especially a cationic compound because these have a strong affinity for anionic dyes), anti-oxidants, polymers (including water-soluble polymers such as polyvinyl pyrrolidone and polyvinyl alcohol), rheology modifiers, and UV-stabilisers, in addition to components (a) to (c).

Optionally the microemulsion contains a block copolymer comprising hydrophobic and hydrophilic units. The hydrophobic units are preferably polyalkane (especially poly C_{2-8}-alkane) or polystyrene. The hydrophilic units are preferably non-ionic units, more

preferably poly(alkylene oxide) units, especially poly(C_{2-5}-alkylene oxide) units, more especially poly(ethylene oxide) units.

The block copolymer preferably has a number average molecular weight of from 500 to 500,000, more preferably 1000 to 100,000, especially 1000 to 50,000.

Particularly preferred block copolymers comprising hydrophobic and hydrophilic units include poly(ethylenepropylene)-block-poly(ethylene oxide) block copolymers and poly(ethylethylene)-block-poly(ethylene oxide) block copolymers.

Suitable block copolymers comprising hydrophobic and hydrophilic units are described in Langmuir, 1999, 15, pp 6707-6711 and Macromolecules, 1996, 29, pp 6994-7002.

The preference for the presence of these block copolymers arises because they allow the microemulsion to be prepared using very low levels of the surfactant. There appears to be a synergistic effect resulting from the combined use of a surfactant and the block copolymer, the mechanism of which is not fully understood. As the surfactant is usually the most expensive component of the microemulsion the presence of the block copolymer can result in large cost savings. The presence of large amounts of surfactant in some circumstances may have a detrimental effect on the coatings properties e.g. causing surface tack and haziness to the curved film.

In one embodiment the microemulsion is free from porous inorganic compounds. The inherently porous nature of the polymer layer can make the presence of such compounds unnecessary.

The microemulsion is preferably applied to the support material by a coating method, for example by dipping, spraying, knife coating, rotogravure coating, reverse roller coating or the like. Preferably the microemulsion is photopolymerisable.

The microemulsion is preferably polymerisable by means of free-radical initiated polymerisation or by means of a polymerisation process which does not involve free-radical initiation. In any case, the microemulsion is preferably thermally or, more preferably, photo-polymerisable (including polymerisable by electron beam or gamma (e.g. Cobalt 60) irradiation). The preference for the microemulsion being photo-polymerisable arises because this enables particularly fast formation of the porous polymer layer. Preferred polymerisation processes which do not involve free-radical initiation include cationic, anionic and condensation polymerisation. Interfacial polymerisation may also be used.

When it is desired to accelerate removal of water from the polymerised microemulsion this may be performed by the application of heat and/or a vacuum thereto. Heat may be applied by any suitable method, including microwave and infra red irradiation. If desired the rate of drying may be controlled by appropriate adjustment of the humidity.

As examples of suitable polymerisable oils (with which the co-polymerisable surfactant may co-polymerise) there may be mentioned inter alia ethylenically unsaturated compounds, including alkyl(meth)acrylates, optionally substituted styrenes, methacrylamides, allyl compounds, vinyl ethers, vinyl ketones, vinyl halides, olefins, unsaturated nitriles and mixtures comprising two or more of the foregoing. The polymerisable oils may also be polymerisable monomers which are not ethylenically unsaturated, either containing or free from ethylenically unsaturated compounds, especially when the polymerisation technique used to obtain the porous polymer layer from the microemulsion comprises electron beam polymerisation.

The polymerisable oil preferably contains one or more ethylenically unsaturated compounds which carry two or more (especially two to six) ethylenically unsaturated groups because this enables the microemulsion to form a cross-linked porous polymer layer with improved mechanical properties. The ethylenically unsaturated groups in such species may be the same as each other (as in diacrylates, triacrylates and divinyl compounds) or they may be different from each other (as in allyl (meth)acrylates). Examples of polymerisable oils which contain two or more ethylenically unsaturated groups include diallylphthalate, divinylbenzene, allyl (meth)acrylate, trimethylol propane tri(meth)acrylate, ethylene glycol di(meth)acrylate, 1,6 hexane diol di(meth)acrylate, dipropylene glycol di(meth)acrylate, diallyl benzene and urethane, polyester, alkyd and epoxy di- and poly-(meth)acrylates.

In one embodiement the polymerisable oil contains one or more ethylenically unsaturated compounds which carry a cationic or anionic group, in this way the cationic or anionic group is capable of forming an ionic bond with a colorant carrying the opposite charge with resultant improvements in the wet-fastness properties of the substrate. Cationic groups are preferred, especially optionally substituted ammonium groups, because these can improve the wet fastness of images on the substrate formed from commonly used anionic dyes due to the attraction between the positive and negative charges.

In one embodiement the alkyl(meth)acrylates contain less than twenty carbon atoms and in another they are oligomers carrying one or more (meth)acrylate groups. Examples of alkyl(meth)acrylates containing less than twenty carbon atoms include methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, sec-butyl acrylate, amyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, octyl acrylate, tert-octyl acrylate, 2-phenoxyethyl acrylate, di- and tripropylene glycol diacrylate, 2-chloroethyl acrylate, 2-bromoethyl acrylate, 4-chlorobutyl acrylate, cyanoethyl acrylate, 2-acetoxyethyl acrylate, dimethylaminoethyl acrylate, benzyl acrylate, methoxybenzyl acrylate, 2-chlorocyclohexyl acrylate, cyclohexyl acrylate, furfuryl acrylate, tetrahydrofurfuryl acrylate, phenyl acrylate, hydroxyethyl(methyl)acrylate,

hydroxypropyl(meth) acrylate, 5-hydroxypentyl acrylate, 2,2-dimethyl-3-hydoxypropyl acrylate, 2-methoxyethyl acrylate, 3-methoxybutyl acrylate, 2-ethoxyethyl acrylate, 2-iso-propoxyethyl acrylate, 2-butyloxyethyl acrylate, 2-(2-methoxyethoxy)ethyl acrylate, 2-(2-butoxyethoxy)ethyl acrylate, 1-bromo-2-methoxyethyl acrylate, 1,1-dichloro-2-ethoxyethyl acrylate, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, sec-butyl methacrylate, amyl methacrylate, hexyl methacrylate, cyclohexyl methacrylate benzylmethacrylate, chlorobenzyl methacrylate, octyl methacrylate, N-ethyl-N-phenylaminoethyl methacrylate, 2-(3-phenylpropyloxy)ethyl methacrylate, dimethylaminophenoxyethyl methacrylate and furfuryl methacrylate.

Preferred oligomers carrying one or more (meth)acrylate groups have a number average molecular weight of from 200 to 50,000, more preferably from 500 to 10,000. Such oligomers are preferably urethanes, polyethers, polyesters, epoxys or alkyds or a hybrid thereof. These oligomers carrying (meth)acrylate groups have an advantage of low volatility, making preparation of the porous polymer layer easier and making them more environmentally friendly than volatile monomers.

Preferred optionally substituted styrenes include styrene, divinyl benzene, methylstyrene, dimethylstyrene, trimethylstyrene, ethylstyrene, diethylstyrene, isopropylstyrene, butylstyrene, hexylstyrene, cyclohexylstyrene, decylstyrene, chloromethylstyrene, trifluoromethylstyrene, ethoxymethylstyrene, acetoxymethylstyrene, methoxystyrene, 4-methoxy-3-methylstyrene, dimethoxystyrene, chlorostyrene, dichlorostyrene, trichlorostyrene, tetrachlorostyrene, pentachlorostyrene, bromostyrene, dibromostyrene, iodostyrene, trifluorostyrene and 2-bromo-4-tri-fluoromethylstyrene.

Preferred methacrylamides contain less than 12 carbon atoms. Examples include methylmethacrylamide, tert-butylmethacrylamide, tert-octylmethacrylamide, benzylmethacrylamide, cyclohexylmethacrylamide, phenylmethacrylamide, dimethylmethacrylamide, dipropylmethacrylamide, hydroxyethyl-N-methylmethacrylamide, N-methylphenylmethacrylamide, N-ethyl-N-phenylmethacrylamide and methacrylhydrazine.

Preferred allyl compounds include allyl acetate, allyl caproate, allyl caprylate, allyl laurate, allyl palmitate, allyl stearate, allyl benzoate, allyl acetoacetate, allyl lactate, allyloxyethanol, allyl butyl ether and allyl phenyl ether.

Preferred vinyl ethers contain less than 20 carbon atoms. Examples include methyl vinyl ether, butyl vinyl ether, hexyl vinyl ether, octyl vinyl ether, decyl vinyl ether, ethylhexyl vinyl ether, methoxyethyl vinyl ether, ethoxyethyl vinyl ether, chloroethyl vinyl ether, 1-methyl-2,2-dimethylpropyl vinyl ether, 2-ethylbutyl vinyl ether, hydroxyethyl vinyl ether and dimethylaminoethyl vinyl ether.

Preferred vinyl ketones contain less than 12 carbon atoms. Examples include methyl vinyl ketone, phenyl vinyl ketone and methoxyethyl vinyl ketone.

Preferred vinyl halides include vinyl chloride, vinylidene chloride and chlorotrifluoro ethylene.

Preferred olefins include unsaturated hydrocarbons having less than 20 carbon atoms. Examples include dicyclopentadiene, ethylene, propylene, 1-butene,1-pentene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-decene, 5-methyl-1-nonene, 5,5-dimethyl-1-octene, 4-methyl-1-hexene, 4,4-dimethyl-1-pentene, 5-methyl-1-hexene, 4-methyl-1-heptene, 5-methyl-1-heptene, 4,4-dimethyl-1-hexene, 5,5,6-trimethyl-1-heptene, 1-dodecene and 1-octadecene.

Preferred unsaturated nitriles include acrylonitrile and methacrylonitrile.

The preferred ethylenically unsaturated compounds are the alkyl (meth)acrylates containing less than 20 carbon atoms, especially those specifically listed above.

The temperature at which polymerisation is carried out may affect the structure of the porous polymer layer. It is often preferred that polymerisation is carried out at about room temperature, e.g. with a photo-initiator, to retain the desired porous structure. Occasionally the presence of a photoinitiator can cause a slight haziness in the micoemulsion and such microemulsions are included within the scope of this invention.

It is often preferred that the polymerisable oil comprises more than one addition-polymerisable water-immiscible organic compound.

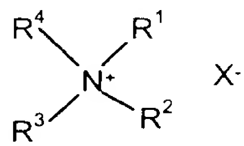
Preferably the polymerisation is performed under conditions such that the configuration of the microemulsion is retained during the polymerisation. Preferably a polymerisable oil is used which results in the porous layer having a Tg above room temperature and/or is cross-linkable with a suitable monomer in the reaction mixture used in the method to give rigidity to the porous layer.

The co-polymerisable surfactant is preferably a non-ionic, anionic, zwitterionic or preferably cationic co-polymerisable surfactant, e.g. a quaternary ammonium compound or a tertiary amine salt.

The preference for cationic co-polymerisable surfactants arises because these result in porous layers with cationic groups having an affinity for anionic dyes commonly used in ink jet printing inks. In this way the wet-fastness properties of the substrate are enhanced by the attraction between the positive cationic groups in the porous layer and the negative anionic groups in the dye.

The co-polymerisable surfactant is co-polymerisable with itself and preferably with at least one other components of the polymerisable oil, for example the co-polymerisable surfactant is capable of grafting onto the polymerisable oil (e.g. by containing a hydrogen atom which is capable of being abstracted during free radical polymerisation) or it is an

addition-polymerisable surfactant. Preferred addition-polymerisable surfactants are of the general Formula:



wherein:

X^- is an anion;

R^1 and R^2 are each independently a C_{1-5}-alkyl group; and

R^3 and R^4 are each independently a C_{1-30}-alkyl group;

with the proviso that at least one of R^1, R^2, R^3 and R^4 carries an ethylenically unsaturated group.

X^- is preferably an inorganic anion, more preferably a halide and especially bromide or chloride.

R^1 and R^2 are preferably methyl.

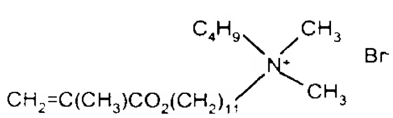
R^3 is preferably C_{1-20}-alkyl.

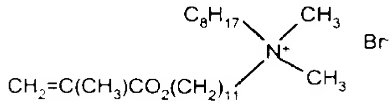
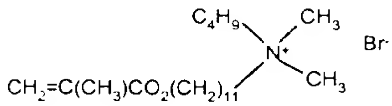
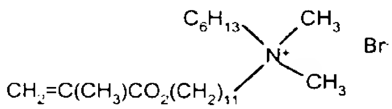
Preferably R^4 is a chain of from 5 to 15 carbon atoms, more preferably about eleven carbon atoms, bearing an ethylenically unsaturated group.

The ethylenically unsaturated group on the addition-polymerisable surfactant is preferably a (meth)acrylate, or an alternative olefinic group, e.g. an alkene or styrene.

The ethylenically unsaturated group on the addition-polymerisable surfactant may be present adjacent the cation, where the surfactant is cationic, although it is often preferred that it is distant therefrom.

The addition-polymerisable surfactant will be chosen in the light of inter alia the chemical properties, particularly hydrophobicity, of the polymerisable oil. For example, as the polarity of the oil is decreased the hydrophobicity of the addition-polymerisable surfactant can often be increased. We have found that the following combinations of surfactant and polymerisable oil are particularly useful in the microemulsions:

Surfactant	Polymerisable Oil
	t-butyl methacrylate

	dodecyl methacrylate
	styrene
	t-butyl-styrene

Whereas we do not exclude the possibility that the polymerisable oil and the addition-polymerisable surfactant may separately homopolymerise during preparation of the ink receptive substrate, it is preferred that they are co- polymerisable.

We do not exclude the possibility that a further surfactant which is non-polymerisable, e.g. $(C_{12}H_{25})_2N^+(CH_3)_2Br^-$, may be present. Preferred further surfactants are co-surfactants, especially linear alcohols, for example C_{4-20}-linear alcohols. Examples of preferred linear alcohols include decanol, octanol and pentanol. The identity and amount of the non-polymerisable surfactant will be chosen to ensure a microemulsion results. It is preferred that a major portion (i.e. more than 50% w/w) of the surfactant is polymerisable.

The free-radical initiator is preferably a photo-initiator, thermal-initiator, a redox initiator or combination thereof.

Preferred photo-initiators consist of a single compound or may comprise at least two components. Typically, the photo-initiator comprises any of the known photo-initiator systems which are used to initiate addition-polymerisation of polymerisable olefinically-unsaturated monomers. As examples of such compositions may be mentioned inter alia (a) mixtures of Michler's ketone and benzil or preferably benzophenone, typically in a weight ratio of about 1:4; (b) the coumarin-based photo-initiator systems described in U.S. Pat. No. 4,289,844; (c) combinations of hexaarylbisimidazoles and leuco dyes; (d) cyclohexadiene-leuco dye systems described in U.S. Pat. No. 4,241,869; (e) systems based on dimethoxyphenylacetophenone (benzil dimethyl ketal) and/or diethoxyacetophenone; or (f) preferably mixtures of amines and ketones as disclosed in UK Patent Specifications Nos 1,408,265 and 1,494,903, e.g. camphorquinone, flurenone or morpholine and N,N-dimethylaminoethyl methacrylate, typically in a weight ratio of about 1:1; (g) mixtures of (i) a light-sensitive initiator system, e.g. an alpha.-diketone, a reducing agent capable of reducing the ketone when the latter is in an excited state, e.g. an organic amine, and (ii) a peroxide, as disclosed in European Patent Specifications Nos

0,059,649, and 0,090,493, the disclosures in which are incorporated herein by way of reference; e.g. a photo-initiator composition comprising camphorquinone, N,N'-dimethylaminoethyl methacrylate and tert-butyl perbenzoate, preferably in the weight ratio about 1:1:1; and (h) photo-initiators which generate acid when irradiated, e.g. aryl diazonium compounds, diaryliodonium compounds, triaryl sulphonium and triaryl selenonium compounds.

The ketone may, for example, be present in the microemulsion in the concentration 0.1% to 2% by weight of the addition-polymerisable material therein although concentrations outside this range may be used if desired. Preferably the alpha-diketone is present in a concentration of 0.1% to 1% by weight of the addition-polymerisable materials in the microemulsion.

The ketones are preferably soluble in the polymerisable material, and the above concentrations refer to solution concentrations.

Preferred thermal-initiators are organic peroxides and thermally decomposable azo compounds, e.g. azo diisobutyronitrile. The organic peroxides, when present in the microemulsion, include those having the formula R^5-O-O-R^5 in which each R^5 independently is hydrogen, alkyl, aryl, or an acyl group, provided that no more than one of the R^5 groups is hydrogen. The term acyl means groups having the formula R^6 -CO- in which R^6 is an alkyl, aryl, alkoxy or aryloxy group. The terms alkyl and aryl include substituted alkyl and aryl.

Examples of organic peroxides suitable for use in the method of the present invention include diacetyl peroxide, dibenzoyl peroxide, ditertiary butyl peroxide, dilauroyl peroxide, tertiary-butyl perbenzoate, ditertiary-butyl-cyclohexyl perdicarbonate.

The organic peroxide may be, for example, present in the microemulsion in the range 0.1% to 20%, preferably 0.5% to 5%, by weight of the polymerisable material in the microemulsion although concentrations outside this range may be used if desired.
The reactivity of a peroxide is often measured in terms of its half-life temperature, i.e. within ten hours at that temperature half of the oxygen has been made available. The peroxides suitable for use in the method according to the present invention preferably have ten-hour half-life temperatures of less than 150 °C more preferably less than 110°C.

According to a second aspect of the present invention there is provided a process for preparing an ink receptive substrate carrying a desired image comprising applying an ink to an ink receptive substrate to give the desired image, wherein the ink receptive substrate is as defined in the first aspect of the invention. The process for preparing an ink receptive substrate carrying a desired image comprises the steps:

(a) applying a polymerisable microemulsion to a support material;

(b) polymerising the product of step (a) to give an ink receptive substrate; and

(c) applying an ink to the ink receptive substrate to give the desired image;

wherein the microemulsion comprises a co-polymerisable surfactant.

The preferred microemulsions, support materials and substrates are as hereinbefore described in relation to the first aspect of the present invention.

The ink is preferably applied in step (c) by a printing method, more preferably by means of an ink jet printer.

The ink jet printer preferably applies an ink to the substrate in the form of droplets which are ejected through a small nozzle onto the substrate. Preferred ink jet printers are piezoelectric ink jet printers and thermal ink jet printers. In thermal ink jet printers, programmed pulses of heat are applied to the ink in a reservoir by means of a resistor adjacent to the nozzle, thereby causing the ink to be ejected in the form of small droplets directed towards the substrate during relative movement between the substrate and the nozzle. In piezoelectric ink jet printers the oscillation of a small crystal causes ejection of the ink from the nozzle.

In a preferred embodiment the product of step (b) is dried before performing step (c). Furthermore, further layers and treatments may be applied to the product of step (b) before and/or after step (c) has been performed, for example a scratch resistant layer.

The ink preferably comprises a colorant and a liquid medium. The ink may also be a liquid toner. Preferred colorants carry anionic groups, especially sulphonate and/or carboxylate groups. Preferred liquid media are water, organic solvent and mixtures comprising water and organic solvent.

The colorant is preferably yellow, magenta, cyan or black.

The colorant may be a single coloured component or a mixture of coloured components, for example it may be a mixture of different dyes. Preferred colorants are dyes, especially anionic dyes, and carbon black pigments (especially the chemically modified carbon black pigments carrying ionic groups available from Cabot Corporation). By using a mixture of different dyes as the colorant one may achieve greater flexibility in colour of the ink.

Useful classes of colorants include anthraquinones, phthalocyanines, pyrrolines, triphenodioxazines, methines, benzodifuranones, coumarins, idoanilines, benzenoids, xanthenes, phenazines, solvent soluble sulphur dyes, quinophthalones, pyridones, aminopyrazoles, pyrollidines, styrylics and azoics. Examples of preferred azo colorants are monoazo, disazo and trisazo disperse dyes each, of which are optionally metallised and solvent soluble dyes; especially preferred azoics contain hetercylic groups. The Colour Index International lists suitable colorants. Preferably the colorant carries one or more anionic groups.

Preferably the ink has been filtered through a filter having a mean pore size of less than 5μm, more preferably less than 2μm. A viscosity of less than 20cp, more preferably less than 10cp, at 20°C is preferred for the ink.

Preferably the ink receptive substrate has an overall thickness of less than 1cm, more preferably less than 2mm, especially less than 0.5mm.

Preferably the porous layer has a void volume of 5 to 75%, more preferably 10 to 60%.

The support material may itself comprise plurality of layers, adhesives and any other properties or features typically found in media. Multi-layer supports are commonly used in the art. In addition the ink receptive substrate may also carry one or more further layers, e.g. a scratch resistant layer, covering the porous polymer layer.

The ink receptive substrates may comprise several layers having differing mean pore sizes and/or void volumes. For example the outermost layer may have a larger mean pore size than the next layer. In this way the relatively large pores of the outermost layer can be made suitable for receiving pigment particles and the next layer is suitable for receiving dye. Furthermore, the ink receptive substrate may contain a further inner layer for receiving the liquid media of an ink to accelerate drying. This can be thought of as a 'solvent sink' to make the media feel dry to the touch quickly and allow ink jet printers to work at high speed without printed substrates being smudged by subsequently printed substrates. Alternatively the substrate may be a fibrous absorbent material which acts a solvent sink.

The various layers of the ink receptive substrate may each independently be neutral, positively charged or negatively charged. Also the size of charge in the layers may be different, e.g. a slightly positive charge on the outer layer and a more positively charged next layer.

The support material is preferably a paper, extruded paper, an opaque or transparent film or foil, especially those made of polyester, polycarbonate, polypropylene, triacetate, polyvinylchloride, etc.

The ink receptive substrates of the invention benefit from fast drying times, avoidance of flammable and toxic organic solvents and good drop definition with little side-ways spread of the image. Furthermore, because inks are fixed in the capillaries of the micro-porous layer, an excellent, durable resolution capability of the substrate may be achieved.

The ink receptive substrate can be used for all presently known recording technologies (e.g. for posters, transparencies, photo-realistic printing, slides, etc.). The substrate can also be used, for instance, for a manual drawing, e.g. by a felt marker, ball-point writing utensil, by plotter apparatuses such as pin-plotters or ink jet-plotters or -printers, respectively, with CAD-recording apparatuses. The ink receptive substrate is particularly useful for photo-realistic printing, especially by ink jet.

In a third embodiment of the present invention there is provided a kit comprising:

(i) an ink receptive substrate comprising a support material and a porous polymer, wherein the porous polymer layer has been obtained by polymerisation of a microemulsion; and

(ii) written instructions to print the substrate with an ink.

Preferably the ink receptive substrate is as defined in the first aspect of the present invention.

Preferably the instructions are written on packaging containing the ink receptive substrate and/or on a sheet of paper accompanying the ink receptive substrate.

The written instructions are preferably for printing the substrate with an ink by means of an ink jet printer. The ink is preferably as hereinbefore described.

The following examples illustrate but do not limit the invention.

Examples 1 to 7 and Controls A to D

Step 1 - Preparation of Microemulsions and Control Examples

Microemulsions and Control Examples were prepared by adding the components indicated in Tables 1 to 4 to 14ml clear glass vials and subsequently rotating the vials on rollers for 24 hours.

The following abbreviations are used in Tables 1 to 3:

C3/11-M	is butyldimethyl-[11-(2 methylacryloloxy)undecyl]ammonium bromide
DPGDA	is dipropyleneglycol diacrylate
HDDA	is hexanediol diacrylate
C12/2-M	is dodecyldimethyl-(2-isopropenyloxycarbonyl ether)ammonium bromide
AUMAB	is trimethylammoniumundecylacrylate bromide
PUD	is the potassium salt of undecanoic acid

Darocur™ 1173 is 2-hydroxy-2-methyl-1-phenyl propan-1-one (Darocur™ is a registered trade mark of Ciba Specialty Chemicals).

The composition of the microemulsions and Control Examples are shown in Tables 1 to 3 below.

Table 1

Component	Weight (g)		
	Example 1	**Control A**	**Control B**
C3/11-M	2.5	5.0	5.0
DPGDA	2.5		5.0
HDDA		5.0	
Water	5.0		
Darocur™ 1173	0.2	0.4	0.4

Table 2

Component	Weight (g)				
	Example 2	**Example 3**	**Example 4**	**Example 5**	**Control C**
HDDA	1.17	0.83	0.5	0.2	2.0
C12/2-M	5.83	4.17	2.5	1.0	
Water	3.0	5.0	7.0	8.8	
Darocur™ 1173	0.28	0.2	0.12	0.05	0.04

Table 3

Component	Weight (g)		
	Example 6	**Example 7**	**Control D**
AUMAB	2.17	1.90	
DPGDA	1.77	1.57	2.0
Water	0.99	1.48	
Darocur™ 1173	0.16	0.14	0.04

Step 2 - Preparation of Ink Receptive Substrates

The microemulsions and Control Examples prepared in step 1 were coated onto a support material (Melinex grade 505) using a Number 5 Meyer bar and then polymerised in a UV Parker box and finally dried in a vacuum oven at 60°C for 1 hour. The appearance of the initial microemulsion or control mixture and the resultant polymer layers is noted in Tables 5 to 8 below.

Step 3 - Ink Jet Printing the Ink Receptive Substrates

The ink receptive substrates resulting from Step 2 were printed on using a HP890 printer loaded with the standard aqueous inks containing anionic dyes and a black pigment ink. The printer was set at the HP transparency print setting. Dry-time was assessed by finger rub and scored according to the following scale:

Score	Dry-Time
5	<15s
4	15s-59s
3	1minute to 1 minute & 59 seconds
2	2-15 minutes
1	>15 -30 minutes
0	>30 minutes

The printed ink receptive substrates were left overnight then a small sample was taken and placed in water. The wet-fastness of the prints was noted after 4 hours (5 excellent, 0 poor). The prints were also assessed for print quality (5 excellent, 0 poor) by visual inspection.

<u>The results of the tests described above on Examples 1 to 7 and Control Examples A to D are described in Tables </u>4 to 6 below.

<u>Table 4</u>

Example	Microemulsion Appearance	Film Appearance	Dry time	Print Quality	Print Appearance	Wet-fastness
1	slight haze #	clear	4	3	gloss	5
Control A	slight haze #	clear	1	3	gloss	4
Control B	slight haze #	clear	1	3	gloss	4

= slight haze caused by photoinitiator.

<u>Table 5</u>

Example	Microemulsion Appearance	Film Appearance	Dry time	Print Quality	Print Appearance	Wet-fastness
2	clear	translucent	0	1	slight gloss	4
3	clear	opaque	3	2	matt	5
4	clear	opaque	5	4	slight matt	5
5	clear	translucent	0	0	slight gloss	3
Control C	clear	clear	0	0	gloss	0

Table 6

Example	Microemulsion Appearance	Film Appearance	Dry time	Print Quality	Print Appearance	Wet-fastness
6	clear	translucent	1	3	gloss	4
7	clear	translucent	2	3	gloss	4
Control D	clear	clear	0	0	gloss	0

The results in Tables 4 to 6 show that the ink receptive substrates prepared using a microemulsion rather than an oil phase composition display significant advantages in their properties.

Example 9

Step 1

A microemulsion was formed by mixing a surfactant (C3/11-M, 6g), polymerisable oil (DPGDA, 4g), water (10g) and a photo-initiator (Darocur™ 1173, 0.4g) until a fluid, transparent microemulsion was formed. This was coated onto a support material (Melinex D706 film) using a No. 3 Wire K-bar to give a 20 micron thick wet film. The microemulsion was then polymerised using a Primarc Minicure UV Station (curing energy ~ $4Jm^{-2}$). The resulting material was a transparent, tack-free solid coated film. This was then dried under vacuo for 2 hours at 50°C to give an ink receptive substrate according to the invention.

Step 2 - Control

A mixture of C3/11-M (6g), DPGDA (4g) and Darocur™ 1173 (0.4g) (NB no water) was coated onto a support material and cured as described in step 1 above to form a control substrate for comparison purposes.

Step 3 Printing and Image Quality

A photographic image was then printed onto the two substrates resulting from Steps 1 and 2 using a HP 890 ink-jet printer loaded with the standard aqueous inks containing anionic dyes and a black pigment ink. The printer was set on the plain paper setting. Dry-time was assessed by finger rub, print quality by visual inspection and water resistance by running tap water over the films for 2 minutes (10= no colour loss evident, 0=colourant completely removed) using the methods described above. The following results were obtained for the substrates resulting from Steps 1 and 2:

	Dry-time (Sec)	Print Quality	Water Resistance
Step 1	<15	Excellent	10
Control (Step 2)	did not dry	Poor	0